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Title: Effects of Heat-Treatment Temperatures and Duration on Critical-Current Densities of Internal-Tin-Processed High-Sn Nb_3Sn Wires

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Effects of Heat-Treatment Temperatures and Duration on Critical-Current Densities of Internal-Tin-Processed High-Sn Nb_3Sn Wires

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Summary:

1) This particular year-2000-vintage high-Sn Nb_3Sn wire, which was fabricated by Oxford Superconducting Technology, is very robust against significant variations in heat-treatment schedules for retaining critical-current densities J_c greater than 2200 A/mm^2 at 12 T and 4.2 K. This is possible as long as an intermediate heat treatment is used, and its temperature is kept well below 500°C. 2) Metallurgical observations of quenched wires after various heat treatments suggest that large interfilamentary spacing in larger-diameter wires help faster Sn diffusion into the filament region. This will help to avoid or minimize the formation of the high-Sn Nb-Sn, compound, e.g., $NbSn_2$, at the inside edge of Nb filamentary region. Since these compounds tend to slow Sn diffusion into the filamentary region, avoiding this compound formation will help to diffuse Sn more uniformly prior to the Nb_3Sn formation. Further, this may increase J_c and/or to shorten the necessary heat-treatment duration.

Purpose:

Heat-treatment schedules for the Nb_3Sn wire were explored to see whether it was possible to ascertain the conditions for increased critical-current densities of the wire or for reduced heat-treatment duration achieving the same J_c which was already obtained.

Experiments:

The wire which was used in this study was fabricated by OST, and consisted of 19 so-called sub-elements in a 0.7- and 1.6-mm-diameter Cu matrix. Each sub-element contained a central Sn core, and fine Nb filaments in a Cu matrix surrounding the core. Also, each sub-element was surrounded by a Nb foil which acted as a diffusion barrier to avoid the diffusion of Sn from the core into the main Cu matrix of the wire. Using this wire, two types of heat treatments were performed: 1) segments of the 0.7-mm wire were mounted on so-called ITER-type mandrels and heat treated to completion for critical current tests, and 2) short and straight segments of the 0.7- and 1.6-mm wire were heat treated and quenched after various durations at different temperatures for microstructural observations of the phase compositional development.

In the first case, a few preliminary experiments were performed to avoid variability in I_c which is related to heat treatments given at different locations as well as to the types of the mandrels used for the reaction. For this purpose, the I_c measurements were made for a pair of the wires which were given the same heat treatment at BNL and OST using Ti alloy mandrels. Also, the wires, which were heat treated at BNL on two types of mandrels, Ti-alloy and stainless steel, were tested for I_c. As shown in Table I, the location of the heat treatment nor the types of the mandrel materials which was used did not cause significant differences in I_c of the wires. The variations in J_c were less than 5 % which is thought to be within the segment-to-segment variations in I_c for this wire. All of the I_c measurements were carried out at OST.

The variations in heat-treatment schedules which were explored were as follows:

a) The intermediate-heat-treatment temperatures and duration: 340°C for 48 and 96 hours, 400°C for 48 and 96 hours, and 500°C for 24 hours.
b) The Nb_3Sn formation heat-treatment temperatures and duration: 650°C for 100 and 180 hours, 675°C for100 hours, and 700°C for 48 hours.
c) Also, a couple of the reaction heat treatments were given without the intermediate treatment, i.e., temperatures were ramped at 100 and 400°C/hour to 650°C and held for 100 h.
d) All of the wire segments for the above tests received a heat treatment of 210°C for 48 hours and the temperature ramp rate was 25°C/h unless otherwise noted.

The second set of the experiments, metallurgical examinations of the quenched wires, were performed to investigate the possible correlation between the observed features, (phase compositions as well as their evolution), and the differences in J_c for the wires with different heat treatments. The wires were quenched from the half-way points and the ends of the intermediate and the reaction heat treatment. Metallurgical observations were also made of the quenched wires having a twice as large wire diameter (1.6 mm) than that (0.7 mm) than for the wires for which J_c was studied. This experiment was to investigate the effects of the enlarged interfilamentary spacing in the rate and in the nature of Sn diffusion from the core to the Nb filamentary region. The interfilamentary spacing would be twice as large in a 1.6-mm wire as in a 0.7-mm diameter wire, but the overall composition and the geometrical construction of the wires are kept the same by using the same wire with different diameters.

Results and discussion:

The results of J_c measurements for these wires are shown in Table II. From these results, it is clear that the effects of variations in the heat-treatment temperature and duration on critical-current densities J_c of this wire are insignificant, and the values of J_c ~ 2200 A/mm^2 at 12 T an 4.2 K are repeatedly reproduced. This was true for both intermediate and final reaction heat-treatment schedules. The variations in J_c seen in Table II are thought to be within the section-to-section variations in J_c. This is only true if the intermediate heat-treatment temperature is kept well below 500°C. When this higher intermediate-heat-treatment-temperature is used, J_c was decreased by ~ 10 % from those above. It is also shown that the intermediate-temperature heat treatment is absolutely necessary for achieving high values of J_c . This is shown by the drastic degradation in J_c of the wires for which the temperature was ramped to the reaction temperature and held at the temperature for 100 hours without the intermediate heat treatment.

The effect of having a 500°C intermediate heat treatment on the microstructure of the wire which was heated through the reaction heat treatment is shown in Fig. (b), and this is compared with that of the wire having an intermediate heat treatment at 400°C in Fig. (a). As shown in Fig. 1 (b), there exists a significant amount of fine particles of Nb_3Sn at the inside portion of the filament region as indicated by the arrows in the figure. These do not contribute to the critical current of the wire, but instead diminish the current-carrying portion of Nb_3Sn. These unattached Nb_3Sn particles appear to originate from the thick $NbSn_2$ ring at the inside portion of the filamentary region of the sub-element. This is shown in Fig. 1(c) for the wire which was heated for 24 h at 500°C and then quenched. When an intermediate temperature, which is substantially lower than 500°C, is used, the thickness of this compound is much less as shown in Fig.2 (a) and (c). Also shown in Fig. 1(d) is the cross section of a wire for which the temperature was ramped to 650°C, and the wire quenched without any intermediate-temperature heat treatment. Again, in this case a large amount of a compound containing Nb, Sn, and Cu was found at the interface between the Sn-Cu core and the filament region. These pre-formed compounds appear to degrade J_c of the high-Sn Nb_3Sn wires when these are in excess as shown.

[Note for those who are not familiar with the Cu-Sn and Nb-Sn phase diagrams for the identification of the phases indicated in Fig. 1 and 2. α is a solid solution Cu-Sn alloy. η and ε are intermetallic compounds having the compositions of ~ Cu-45 at.% Sn. of ~ Cu-25 at.% Sn, respectively. Nb and Sn also form three intermetallic compounds, Nb_3Sn, Nb_6Sn_5, and $NbSn_2$. If Nb and Sn are mixed and heated, all of these compounds are formed. The unique aspect of forming Nb_3Sn by placing Nb filaments in a low-Sn Cu-Sn matrix is to make it possible to form only Nb_3Sn and to avoid the simultaneous formation of two high-Sn compounds. Since the Sn contents of the recent internal-Sn-processed wires are so high that high-Sn Nb-Sn compounds can be formed before Nb_3Sn is formed.]

In general it is thought that Sn in the core should be thoroughly distributed into the filamentary region of the wire before the Nb_3Sn formation begins in order to achieve the highest J_c for a given wire. However, when the wire is reduced to the practical sizes, 0.7 mm, the interfilamentary spacing in the sub-elements becomes so small that the diffusion of Sn into the filament region becomes very slow. Moreover, in these high-Sn wires, the reactivity of Sn in the core is also increased such that the high-Sn Nb-Sn compounds are easily formed at the interface region between the core and the filament region as shown in Fig. 1(c) and 2(a) and (c). These compound rings will further slow the diffusion of Sn to the outer areas of the wire. Thus, we carried out the above mentioned quench experiments in order to see whether this situation can be avoided or minimized by opening up the space between the filaments without changing the overall composition of the wire. Here, we have taken the same wire, which was studied above, but at a larger diameter, 1.6 mm. Both of these wires were heated at and quenched from the intermediate-heat-treatment temperatures. Then the degree of the Sn diffusion from the core to the outer areas was compared for these wires.

These results are shown in Fig. 2 for the wires which were heat for 48 h at 340°C (a) and (b) and at 400°C (c) and (d). As clearly seen in these figures, there are significant differences in the degree of Sn diffusion at these stages of the heat treatments. (1) In both intermediate-heat-treatment temperatures, the smaller wires exhibit the formation of the

$NbSn_2$ compound at the inner portion of the filament package, while there is no indication of such compound formation in the larger wire. (2) Also, there is substantial Sn diffusion into the filament regions in the larger wires depicted in Fig. 2(b) and (d) as indicated by the white arrows, while there is no indication of similar Sn diffusion in Fig. (a) and (c). These observations suggest that very small Nb filamentary spacing not only slows the Sn diffusion in the Cu between the filaments, but also causes the formation of $NbSn_2$ layers to further slow down the Sn diffusion. Thus, the more-uniform Sn diffusion prior to the formation of Nb_3Sn achieved in larger wires may help to achieve a higher J_c in the filaments. Unfortunately, this could not be tested since the critical currents in the larger wire are expected to be at least 4 time higher than the smaller one and this higher current makes the I_c measurements difficult in the present I_c-measurement set-up.

Table I. Comparison of J_c for the Nb_3Sn wires which were heat treated at OST and BNL and on Ti-alloy and stainless steel mandrels.

Temp. (°C) – hours	Temp. (°C) - hours	J_c(A/mm^2) at 12 T	H.T. location - spool
340- 48	650 - 180	2284	BNL - Ti
		2197	OST - Ti
400 - 48	675 - 100	2334	BNL - ss
		2231	BNL - ss
		2400	BNL - ss

Table II Critical current densities J_c of Nb_3Sn wires which were heat treated with various schedules.

Temp. (°C) – hours	Temp. (°C) - hours	J_c(A/mm^2) at 12 T
340 - 48	650 - 100	2303
	650 - 180	2241 ave
340 - 96	650 - 100	2303
	675 - 100	2224
400 - 96	650 - 100	2303
400 - 48	675 - 100	2322 ave
400 - 96	675 - 100	2224
400 - 48	700 - 48	2227
500 - 24	650 - 100	1972
	675 - 100	2087
none	ramped 650 (100 °C/h)	1318
	ramped 650 (400 °C/h) (two each)	0

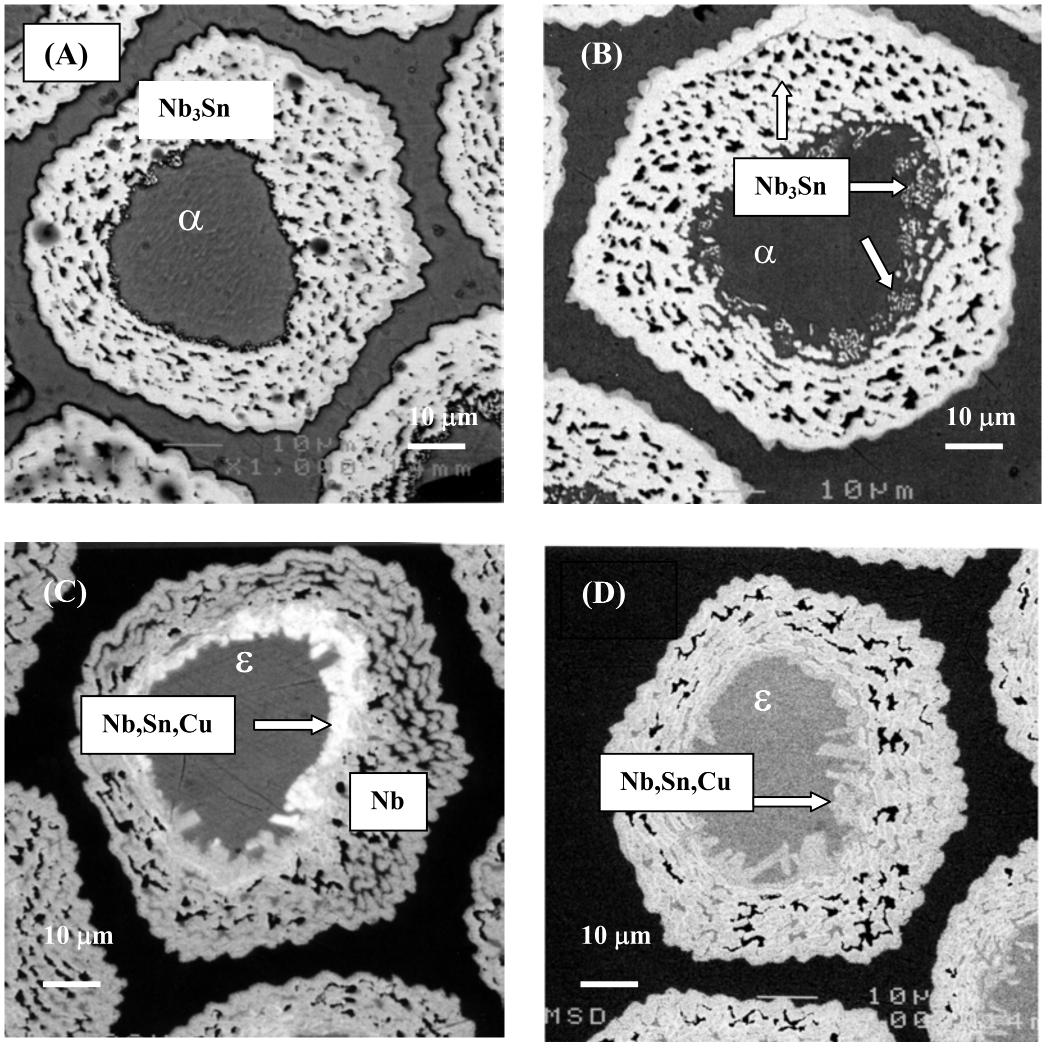

Fig. 1. Cross sectional images of Nb_3Sn wires taken by scanning electron microscopy showing the phase composition of the wire at different stages of heat treatment. These are after being heat treated at (a) 400 °C for 48 h + 675 °C for 100 h, (b) 500 °C for 24 h + 675 °C for 100 h, and (c) quenched after being heated at 500 °C for 24 h, and (d) quenched after temperature was ramped to 650 °C. α is a Cu-Sn solid solution alloy while ε is a Cu-Sn compound with an approximate composition of Cu_3Sn.

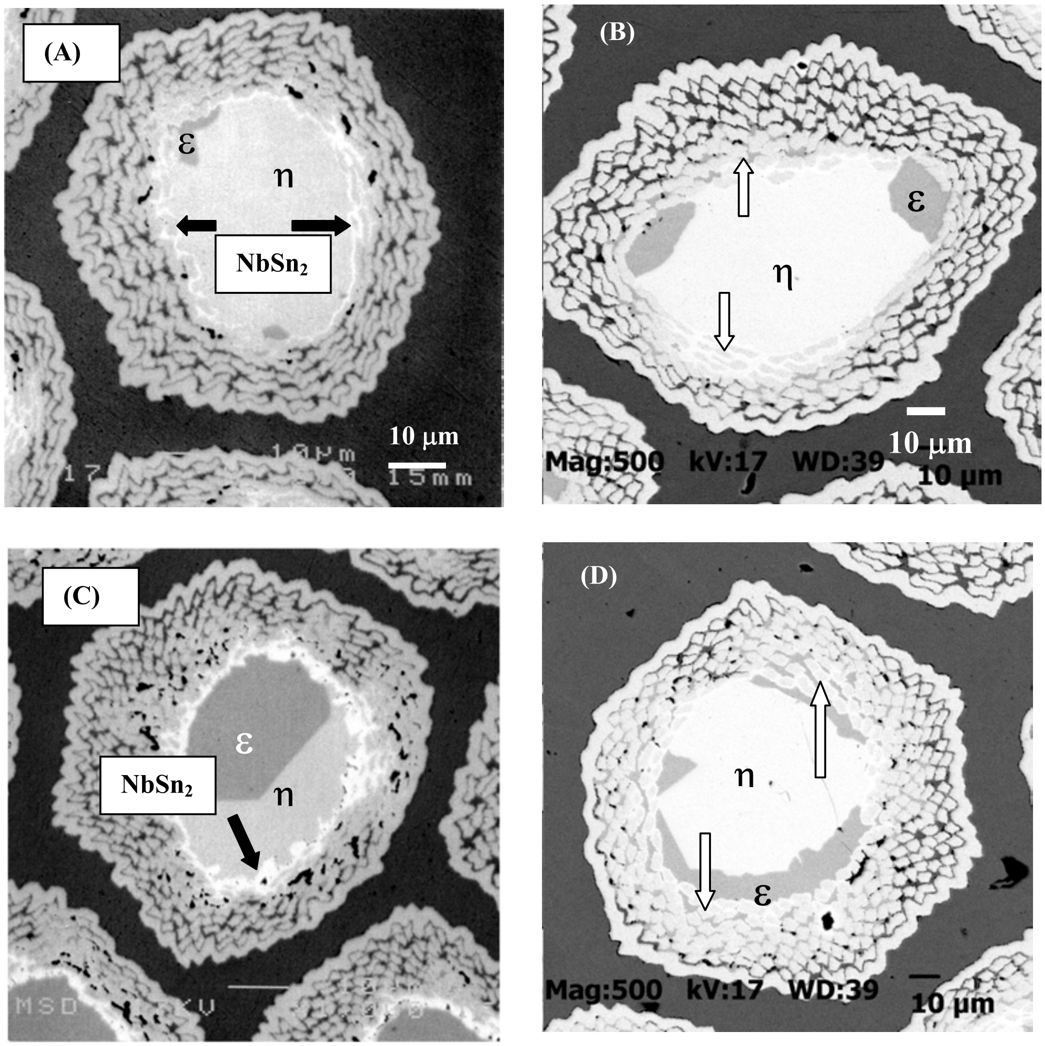

Fig. 2. Cross sectional images of the Nb_3Sn wires by scanning electron microscopy of the wires quenched after being heated for 48 h (a) and (b) at 340 °C and (c) and (d) at 400 °C. The effects of the difference in wire diameters on the Sn diffusion rates into the Nb filament regions are illustrated. The black arrows point to the formation of $NbSn_2$ layers, and the white arrows point to the areas with the diffusion of Sn into the filament regions. The diameters of the wires are 0.7 and 1.6 mm for (a) and (c), and (b) and (d), respectively. η is a Cu-Sn compound with an approximate composition of Cu_6Sn_5.